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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
10/581,607	07/14/2006	Leif Westin	61192	5461

23117 7590 04/16/2008

NIXON & VANDERHYE, PC
901 NORTH GLEBE ROAD, 11TH FLOOR
ARLINGTON, VA 22203

EXAMINER	
VELASQUEZ, VANESSA T	

ART UNIT	PAPER NUMBER
1793	

MAIL DATE	DELIVERY MODE
04/16/2008	PAPER

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Office Action Summary	Application No. 10/581,607	Applicant(s) WESTIN, LEIF	
	Examiner Vanessa Velasquez	Art Unit 1793	

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTH(S) OR THIRTY (30) DAYS, WHICHEVER IS LONGER, FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

1)☒ Responsive to communication(s) filed on *14 July 2006*.

2a)☐ This action is **FINAL**. 2b)☒ This action is non-final.

3)☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims

4)☒ Claim(s) *1-21* is/are pending in the application.

4a) Of the above claim(s) _____ is/are withdrawn from consideration.

5)☐ Claim(s) _____ is/are allowed.

6)☒ Claim(s) *1-8 and 10-21* is/are rejected.

7)☒ Claim(s) *9* is/are objected to.

8)☐ Claim(s) _____ are subject to restriction and/or election requirement.

Application Papers

9)☐ The specification is objected to by the Examiner.

10)☐ The drawing(s) filed on _____ is/are: a)☐ accepted or b)☐ objected to by the Examiner.

Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).

Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).

11)☐ The oath or declaration is objected to by the Examiner. Note the attached Office Action or form PTO-152.

Priority under 35 U.S.C. § 119

12)☒ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

a)☒ All b)☐ Some * c)☐ None of:

1.☐ Certified copies of the priority documents have been received.

2.☐ Certified copies of the priority documents have been received in Application No. _____.

3.☒ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

* See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

1) ☒ Notice of References Cited (PTO-892)

2) ☐ Notice of Draftsperson's Patent Drawing Review (PTO-948)

3) ☒ Information Disclosure Statement(s) (PTO/SB/08) Paper No(s)/Mail Date *June 5, 2006*.

4) ☐ Interview Summary (PTO-413) Paper No(s)/Mail Date. _____.

5) ☐ Notice of Informal Patent Application

6) ☐ Other: _____.

DETAILED ACTION

Status of Claims

Claims 1-21 are pending and presented for examination.

Priority

1. Acknowledgment is made of Applicant's claim for foreign priority under 35 U.S.C. 119(a)-(d). The certified copy of Application No. 0303289-3, filed in Sweden, has been placed of record in the file.

Information Disclosure Statement

2. One (1) information disclosure statement (IDS) was submitted on June 5, 2006. The submission is in compliance with the provisions of 37 CFR 1.97. Accordingly, the information disclosure statement is being considered by the examiner.

Claim Objections

3. Claim 2 is objected to because the amount of residual austenite is not labeled with units. The Examiner will interpret the units to be percent by volume for the purposes of applying prior art. Appropriate correction is required.

4. Claim 9 is objected to under 37 CFR 1.75(c) as being in improper form because a multiple dependent claim cannot depend from any other multiple dependent claim. Specifically, Claim 9 depends on any one of Claims 1-8. Claim 7, however, is also a

multiple dependent claim. See MPEP § 608.01(n). Accordingly, the claim has not been further treated on the merits.

5. Claim 16 is objected to because of a spelling mistake. "Characrterised" should be characterised. Appropriate correction is required.

Claim Rejections - 35 USC § 112, Second Paragraph

6. The following is a quotation of the second paragraph of 35 U.S.C. 112:

> The specification shall conclude with one or more claims particularly pointing out and distinctly claiming the subject matter which the applicant regards as his invention.

7. Claims 1-21 are rejected under 35 U.S.C. 112, second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which applicant regards as the invention.

Regarding Claim 1, the terms "good" and "normal" are relative terms which render the claim indefinite. The terms "good" and "normal" are not defined by the claim, the specification does not provide a standard for ascertaining the requisite degree, and one of ordinary skill in the art would not be reasonably apprised of the scope of the invention. Claims 2-21 are likewise rejected because of their dependency on Claim 1.

Regarding Claim 2, the claim is rendered indefinite because the term "M(N,C)" is not sufficiently defined in the claim itself and/or specification.

Regarding Claims 3-8, 10-12, and 15, Applicant is reminded that a broad range or limitation together with a narrow range or limitation that falls within the broad range or limitation (in the same claim) is considered indefinite, since the resulting claim does not clearly set forth the metes and bounds of the patent protection desired. See MPEP §

2173.05(c). Note the explanation given by the Board of Patent Appeals and Interferences in *Ex parte Wu*, 10 USPQ2d 2031, 2033 (Bd. Pat. App. & Inter. 1989), as to where broad language is followed by "such as" and then narrow language. The Board stated that this can render a claim indefinite by raising a question or doubt as to whether the feature introduced by such language is (a) merely exemplary of the remainder of the claim, and therefore not required, or (b) a required feature of the claims. Note also, for example, the decisions of *Ex parte Steigewald*, 131 USPQ 74 (Bd. App. 1961); *Ex parte Hall*, 83 USPQ 38 (Bd. App. 1948); and *Ex parte Hasche*, 86 USPQ 481 (Bd. App. 1949). Claims 17-21 are likewise rejected because of their dependency on Claim 15.

Regarding Claims 17-21, the claims provide for the use of a steel material, but since the claim does not set forth any steps involved in the method/process, it is unclear what method/process applicant is intending to encompass. A claim is indefinite where it merely recites a use without any active, positive steps delimiting how this use is actually practiced.

Claim Rejections - 35 USC § 101

8. 35 U.S.C. 101 reads as follows:

> Whoever invents or discovers any new and useful process, machine, manufacture, or composition of matter, or any new and useful improvement thereof, may obtain a patent therefor, subject to the conditions and requirements of this title.

Claims 17-21 are rejected under 35 U.S.C. 101 because the claimed recitation of a use, without setting forth any steps involved in the process, results in an improper

definition of a process, i.e., results in a claim which is not a proper process claim under 35 U.S.C. 101. See for example *Ex parte Dunki*, 153 USPQ 678 (Bd.App. 1967) and *Clinical Products, Ltd.* v. *Brenner*, 255 F. Supp. 131, 149 USPQ 475 (D.D.C. 1966).

Claim Rejections - 35 USC § 103

9. The following is a quotation of 35 U.S.C. 103(a) which forms the basis for all obviousness rejections set forth in this Office action:

> (a) A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negatived by the manner in which the invention was made.

10. The factual inquiries set forth in *Graham* **v.** *John Deere Co.*, 383 U.S. 1, 148 USPQ 459 (1966), that are applied for establishing a background for determining obviousness under 35 U.S.C. 103(a) are summarized as follows:

1. Determining the scope and contents of the prior art.
2. Ascertaining the differences between the prior art and the claims at issue.
3. Resolving the level of ordinary skill in the pertinent art.
4. Considering objective evidence present in the application indicating obviousness or nonobviousness.

11. Claims 1, 3-8, 10, 15, and 16 are rejected under 35 U.S.C. 103(a) as being unpatentable over Koga et al. (US 2002/0164260 A1).

Regarding Claims 1 and 3-8, US '260 teaches a corrosion-resistant steel composition comprising the following elements, in percent by weight (US '260, pp. 1-2, para. [0015]):

Carbon	< 0.15

Nitrogen	0.40-0.80
Chromium	12.0-18.5
Manganese	0.10-2.0
Nickel	0.2-3.0
Molybdenum	0.2-4.0
Tungsten	0.020-0.20
Vanadium	0.020-0.20
Niobium	0.020-0.20
Titanium	0.020-0.20
Silicon	0.10-1.0
Cobalt	0.50-4.0
Iron	balance

The overlap of the ranges taught by US ‘260 with the claimed ranges is sufficient to establish a *prima facie* case of obviousness (MPEP § 2144.05).

Still regarding Claim 1 and concerning sulfur, US ‘260 is silent as to the sulfur content. However, sulfur is one of the most common impurities in steel. Therefore, even though US ‘260 fails to explicitly teach sulfur content, at least trace amounts of the element would be expected to be present in the composition disclosed.

Still regarding Claim 1 and concerning the transitional phrase "consists of", the phrase indicates closed language (see MPEP § 2111.03). Although US ‘260 teaches that other elements may be present (Al and O, p. 2, para. [0015], ln. 4-5), the ranges taught encompass zero. Thus, the elements do not necessarily have to be present and

may be omitted to arrive at the claimed composition. In addition, the additional elemental additives (see US '260, p. 2, para. [0015], ln. 5-16) are also optional, as indicated by the phrase "one or more of." Because each additive imparts well-known specific qualities to the finished steel product, it would have been obvious to one of ordinary skill to use those qualities as a guide in selecting a particular combination of additives, as doing so would lead one to arrive at a steel product with a particular set of desired mechanical properties.

Regarding Claim 10, the alloy taught by US '260 fails to teach a Nb in amounts greater than 0.2 wt.%. However, this upper bound applies only if vanadium, tungsten, titanium, tantalum, and zirconium are also **each** 0.2 wt.% in the alloy (US '260, p. 3, para. [0047]). Therefore, if vanadium, tungsten, titanium, tantalum, and zirconium are present in smaller amounts or are not present at all, niobium may be present in an amount exceeding 0.030 wt.% (US '260, p. 3, para. [0047]). One of ordinary skill in the art would be motivated to increase the amount of niobium above the individually taught range of 0.2 wt.% because it functions as a grain refiner, thereby contributing to the strength of the alloy.

Regarding Claims 15 and 16, Applicant is reminded that in product-by-process claims, patentability is based on the product itself. The patentability of a product does not depend on its method of production. If the product in the product-by-process claim is the same as or obvious from the product of the prior art, the claim is unpatentable even though the prior product was made by a different process. (MPEP § 2113)

12. Claims 2, 11, and 12 are rejected under 35 U.S.C. 103(a) as being unpatentable over Koga et al. (US 2002/0164260 A1) in view of Goecmen et al. ("Precipitation Behaviour and Stability of Nitrides in High Nitrogen Martensitic 9% and 12% Chromium Steels," *ISIJ International*, Vol. 36, No. 7, pp. 768-776), and further in view of Webster (US 3,563,813).

Regarding Claim 2, US '260 is silent as to the microstructure of the disclosed alloy. However, Goecmen, also drawn to a high-nitrogen martensitic steel alloy, teaches that MN and chromium-rich M_2N type precipitates are formed in the tempered nitrogen martensite of a chromium steel (Goecmen et al., p. 772). Although Goecmen is silent as to a preferred amount of each phase, it would be obvious to one of ordinary skill in the art to determine optimum amounts through routine experimentation to obtain a product with desired properties. (MPEP § 2144.05) Furthermore, it would have been obvious to one of ordinary skill in the art to combine Goecmen with US '260 because the alloys in Goecmen exhibit enhanced mechanical properties.

Still regarding Claim 2 and concerning the hardness limitation, hardness is affected by the size and spacings of nitride particles (Goecmen, Abstract). Thus, it would have been obvious to one of ordinary skill in the art to precipitate a predetermined number of nitride particles to obtain a product with a desired hardness. (MPEP § 2144.05)

Still regarding Claim 2 and concerning the residual austenite limitation, US '260 in view of Goecmen fail to teach residual austenite in the martensite phase. However, US '813, also drawn to a stainless steel, teaches that the presence of austenite

enhances the toughness of brittle martensite (US '813, col. 1, ln. 41-44). A preferable amount of retained austenite is 5% to 30% (US '813, col. 1, ln. 69 to col. 2, ln. 1-3). Therefore, it would have been obvious to one of ordinary skill in the art to ensure that some austenite remained in the tempered martensite alloy of US '260 in view of Goecmen because austenite improves the toughness of martensitic stainless steels (US '813, col. 1, ln. 36-40).

Regarding Claims 11 and 12, Applicant is reminded that in product-by-process claims, patentability is based on the product itself. The patentability of a product does not depend on its method of production. If the product in the product-by-process claim is the same as or obvious from the product of the prior art, the claim is unpatentable even though the prior product was made by a different process. (MPEP § 2113)

Still regarding Claim 12 and concerning the hardness limitation, hardness is affected by the size and spacings of nitride particles (Goecmen, Abstract). Thus, it would have been obvious to one of ordinary skill in the art to precipitate a predetermined number of nitride particles to obtain a product with a desired hardness. (MPEP § 2144.05)

13. Claims 13 and 14 are rejected under 35 U.S.C. 103(a) as being unpatentable over Koga et al. (US 2002/0164260 A1) in view of Goecmen et al. ("Precipitation Behaviour and Stability of Nitrides in High Nitrogen Martensitic 9% and 12% Chromium Steels," *ISIJ International*, Vol. 36, No. 7, pp. 768-776).

Regarding Claims 13 and 14, US '260 is silent as to the microstructure of the disclosed alloy. However, Goecmen, also drawn to a high-nitrogen martensitic steel alloy, teaches that MN and chromium-rich M_2N type precipitates are formed in the tempered nitrogen martensite of a chromium steel (Goecmen et al., p. 772). Although Goecmen is silent as to the specific elemental constitution of the hard phases (i.e., Cr, Nb, V, Mo, and Fe recited in said claims), the recited elements are well known in the art as carbide- and/or nitride- forming elements. Thus, they would inherently be present in the hard phases. (MPEP § 2112) It would have been obvious to one of ordinary skill in the art to combine Goecmen with US '260 because the alloys in Goecmen exhibit enhanced mechanical properties.

Conclusion

Any inquiry concerning this communication or earlier communications from the examiner should be directed to Vanessa Velasquez whose telephone number is (571)270-3587. The examiner can normally be reached on Monday-Friday 8:30 AM-6:00 PM ET.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Roy King, can be reached at 571-272-1244. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see http://pair-direct.uspto.gov. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free). If you would like assistance from a USPTO Customer Service Representative or access to the automated information system, call 800-786-9199 (IN USA OR CANADA) or 571-272-1000.

/Roy King/
Supervisory Patent Examiner, Art Unit 1793

/Vanessa Velasquez/
Examiner, Art Unit 1793

10/581607
AP3 Rec'd PCT/PTO 05 JUN 2006

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

WESTIN — Atty. Ref.: 611-92

Serial No. Unassigned — TC/A.U.: Unassigned

Filed: June 5, 2006 — Examiner: Unassigned

For: MARTENSITIC CHROMIUM-NITORGEN STEEL AND ITS USE

* * * * * * * * * * *

June 5, 2006

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

INFORMATION DISCLOSURE STATEMENT

Attached is a completed Form PTO/SB/08a listing references in connection with this application. Also enclosed is a copy of each of those references, along with the International Search Report.

The Examiner is requested to initial the attached PTO/SB/08a, and to return a copy of the initialed document to the undersigned as an indication that the listed references have been considered and made of record.

Respectfully submitted,

NIXON & VANDERHYE P.C.

By: ____________________
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INFORMATION DISCLOSURE CITATION

(Use several sheets if necessary)

ATTY. DOCKET NO.	SERIAL NO.
611-92	Unassigned
APPLICANT	
WESTIN	
FILING DATE	TC/A.U.
June 5, 2006	Unassigned

U.S. PATENT DOCUMENTS

*EXAMINER INITIAL		DOCUMENT NUMBER	DATE	NAME	CLASS	SUBCLASS	FILING DATE IF APPROPRIATE
/NTV/		6,673,165	01/2004	Koga et al			

FOREIGN PATENT DOCUMENTS

		DOCUMENT	DATE	COUNTRY	CLASS	SUBCLASS	TRANSLATION YES	NO
/NTV/		EP 1 236 809 A2	09/2002	EP				
/NTV/		EP 0 810 294 A1	12/1997	EP				
/NTV/		DE 42 32 695 A1	03/1994	DE				
/NTV/		DE 3901 470 C1	08/1990	DE				

OTHER DOCUMENTS (including Author, Title, Date, Pertinent pages, etc.)

*Examiner	/Vanessa T Velasquez/	Date Considered	04/09/2008

Examiner: Initial if reference considered, whether or not citation is in conformance with MPEP 609; Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to application.

Notice of References Cited	Application/Control No. 10/581,607	Applicant(s)/Patent Under Reexamination WESTIN, LEIF	
	Examiner Vanessa Velasquez	Art Unit 1793	Page 1 of 1

U.S. PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Name	Classification
*	A	US-2002/0164260	11-2002	Koga et al.	420/61
*	B	US-3,563,813	02-1971		148/578
	C	US-			
	D	US-			
	E	US-			
	F	US-			
	G	US-			
	H	US-			
	I	US-			
	J	US-			
	K	US-			
	L	US-			
	M	US-			

FOREIGN PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Country	Name	Classification
	N					
	O					
	P					
	Q					
	R					
	S					
	T					

NON-PATENT DOCUMENTS

*		Include as applicable: Author, Title Date, Publisher, Edition or Volume, Pertinent Pages)
	U	Goecmen et al., "Precipitation Behaviour and Stability of Nitrides in High Nitrogen Martensitic 9% and 12% Chromium Steels," ISIJ International, Vol. 36, No. 7, 1996, pp. 768-776.
	V	
	W	
	X	

*A copy of this reference is not being furnished with this Office action. (See MPEP § 707.05(a).)
Dates in MM-YYYY format are publication dates. Classifications may be US or foreign.

ISIJ International, Vol. 36 (1996), No. 7, pp. 768–776

Precipitation Behaviour and Stability of Nitrides in High Nitrogen Martensitic 9% and 12% Chromium Steels

Alkan GOECMEN, Reiner STEINS, Christian SOLENTHALER, Peter J. UGGOWITZER and Markus O. SPEIDEL

Swiss Federal Institute of Metallurgy ETH, Sonneggstr. 3, Zurich, Switzerland.

(Received on September 29, 1995; accepted in final form on April 12, 1996)

Precipitation behaviour and stability of nitrides has been investigated in two high nitrogen, high vanadium containing martensitic 9–12% chromium steels under different heat treatment conditions. Microstructural evolution during the heat treatments was studied by hardness measurements, optical microscopy, transmission electron microscopy and energy dispersive X-ray analysis.

Nitrides with f.c.c. structure were found to precipitate very uniformly and densely during aging in the austenite (ausaging) as well as during aging in the ferrite (tempering) at temperatures between 823 and 973 K. Microstructural evolution during tempering was influenced by pre-precipitation of the nitrides in the austenite prior to the martensitic transformation. It is shown that the hardness of martensite and tempered martensite depend strongly on the size and distribution of nitrides. Niobium is dissolved in primary vanadium nitrides. Dissolution and reprecipitation of these nitrides in the austenite was found to be influenced by the presence of niobium. Ausaging treatment of a niobium containing alloy at 898 K has a more significant effect on the martensite hardness than a niobium free alloy.

The stability of dense precipitation states produced in the austenite prior to the martensitic transformation is discussed in terms of the development of non uniform precipitation states during tempering of the martensite. The uniformity of the precipitation states is stabilized by a pre-overaging treatment in the austenite. It is shown for a martensitic 12% chromium alloy, that a pre-ausaging treatment retards the formation of the rapid coarsening hexagonal chromium nitride which dissolves a high amount of vanadium during tempering at 973 K. As a result the tempering resistance becomes improved by maintaining an increased density of face centered cubic nitrides precipitated in the austenite.

KEY WORDS: high nitrogen martensitic 9–12% chromium steels; precipitation behaviour; nitrides; ausaging; tempering; chromium nitrides; particle coarsening.

1. Introduction

Martensitic 9–12% chromium steels belong to the transformation hardened steels.[1] The main source for the strengthening of these steels is offered by a diffusionless phase transformation producing a supersaturated microstructure with a very dense distribution of dislocations and internal surfaces.[2] Beneficial combinations of strength and toughness are achieved by quenchening and subsequent tempering at an intermediate temperature. The resulting microstructure is a complex particle/dislocation substructure in the body centered cubic iron matrix.

The martensitic 9–12% chromium steels are favoured by economical manufacturing as well as by physical and mechanical properties for various high temperature power plant applications.[3,4] Recent extensive development works show that improved combinations of mechanical properties can be achieved by high nitrogen addition combined with a proper choice of alloy composition and heat treatment.[5–8]

Due to the increased demands for application temperatures, the thermal stability of the microstructure resulting from alloy composition and heat treatment is of fundamental interest. Mechanical properties and thermal stability of the microstructures are known to depend strongly on heat treatment, especially on the dissolution behaviour of thermally stable nitrides at high normalizing temperatures.[5–9] Thus the achievable property combinations of structure such as grain size, martensite hardness and tempering resistance depend on the precipitation behaviour and stability of nitrides.

The purpose of this paper is to report the results obtained from microstructural investigations on the precipitation behaviour and stability of nitrides in two different high nitrogen martensitic 9–12% chromium steels and to discuss the microstructural evolution during the heat treatments.

2. Experimental Procedure

Heats of 10 kg were melted in a vacuum induction furnace at temperatures between 1 500 and 1 600°C with an applied nitrogen pressure of 90 kPa during melting

Table 1. Chemical compositions of the investigated steels. (wt%)

	Fe	Cr	Mn	Ni	Co	Ti	V	Nb	Mo	W	Si	N	C
833	bal	9.1	2.9	0.5	—	<0.01	0.66	0.05	0.95	0.45	0.16	0.16	0.006
758	bal	12.1	2.6	0.5	3.4	<0.01	0.76	<0.01	0.46	0.96	0.16	0.18	0.03

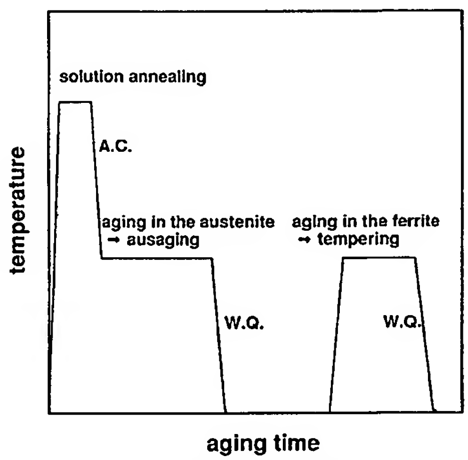


Fig. 1. Schematic representation of heat treatment B: ausaging before martensite formation.

and solidification. Their chemical compositions are given in Table 1. The castings were homogenized at 1 150°C for 5 h and subsequently forged at temperatures ranging from 1 200 to 1 100°C. The microstructures of the specimens of 15 mm thickness were adjusted by two different heat treatments. Heat treatment A is characterized by solution annealing at 1 200°C for 1.5 h with air quenching (normalizing) and a following tempering treatment in the ferrite range. In heat treatment B an additional isothermal aging treatment (ausaging) was applied between the solution annealing and water quenching as schematically represented in **Fig. 1**. The A_{c1} temperature, determined by hardness measurements after 4 h tempering time, lies between 720 and 750°C in both alloys.

Microstructural evolution was recorded with hardness measurements, optical microscopy and transmission electron microscopy (TEM) operating at 120 kV equipped with energy dispersive X-ray analysis (EDX). Thin foils for TEM observations were electrochemically thinned in a 95% acetic acid–5% perchloric acid solution at about 15°C and 250 mA.

3. Experimental Results and Discussions

3.1. Hardness and Microstructure of the As Quenched Martensite

3.1.1. Hardness and Microstructure in the Normalized and Quenched State

Figure 2 shows optical micrographs of the two alloys in normalized and quenched condition. Alloy 833 was fully hardened. About 2–5% δ-ferrite could be observed in alloy 758. The alloys differ markedly with respect to martensite hardness (alloy 833: 400 HV10; alloy 758: 500 HV10) and to the size of the former austenite grain (alloy 833: 30–50 μm; alloy 758: 50–80 μm). As a consequence of the composition and normalizing treatment, part of the alloyed nitrogen is undissolved and remains tied up in coarse primary nitrides with face centered cubic crystal structure (fcc). As observed in TEM investigations the average size of these nitrides is similar in both alloys with an average diameter of about 0.5 to 1 μm. Alloy 833, however, shows a higher volume fraction and a more dense distribution of the undissolved nitrides. The corresponding EDX-spectra of these nitrides are additionally shown in Fig. 2. They differ essentially by the absence of the Nb signal in alloy 758. The finer grain size in the Nb-stabilized alloy 833 is assumed to be resulted from the increased precipitation density of primary nitrides.

3.1.2. Effect of an Ausaging Treatment on the Hardness and Microstructure of the As Quenched Martensite

Figures 3 and **4** show the effect of an ausaging treatment on the hardness of the quenched alloys 833 and 758, respectively. Comparing the effect of ausaging on the martensite hardness of the alloys 758 and 833 one can see that the alloy 833 is precipitation hardening at an ausaging temperature of 898 K whereas alloy 758 starts to soften at an ausaging temperature of 873 K. This difference was found to be resulted from an increased particle growth in the Nb-free alloy 758 during the isothermal ausaging treatment. **Figure 5** shows the corresponding microstructures of alloy 833 after an ausaging treatment at 898 and 973 K. Both states are fully martensitic. Within the temperature and time range of the applied ausaging treatments no direct transformation from austenite into ferrite took place, but always martensitic transformation could be observed. The result of the ausaging experiments therefore suggests that the martensitic transformation hardening is directly influenced by the precipitation hardening of the austenite. Consequently the precipitation states shown in Figs. 5(b) and 5(d) represent the difference between "peak-aged" and "over-aged" precipitation states. The particle depleted zone around the coarse primary nitride shown in Fig. 5(d) further indicates that the same alloying elements must have contributed to the coarse primary nitride as well as to the fine precipitates. The particle hardened martensite shows lath morphology with a typical lath width of 0.3 to 0.5 μm. No complete morphological change from lath to plate martensite caused by the precipitation hardening of the austenite could be observed.[10] However, due to higher volume fraction of precipitates in alloy 758 compared with alloy 833, distinct effects of ausaging on the martensite morphology could be observed as an increased planar distribution of dislocations and "plate-like" extension of

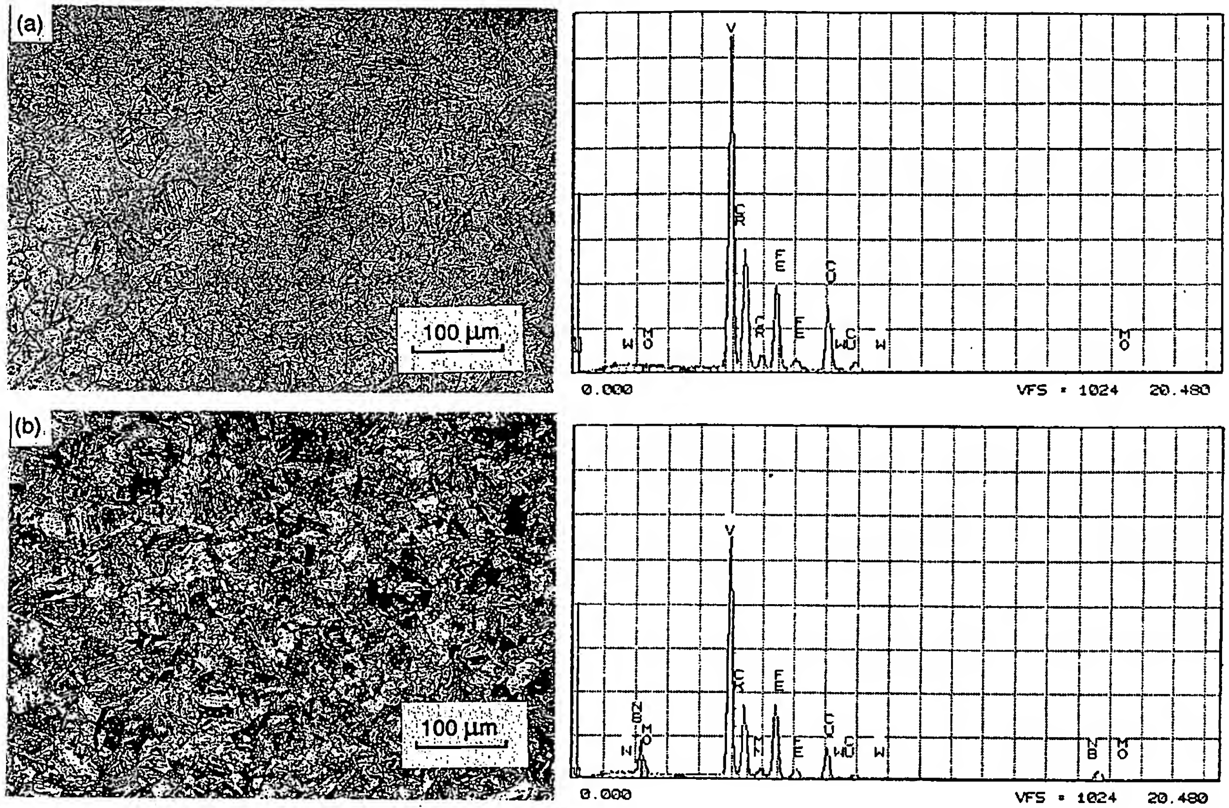


Fig. 2. Optical micrographs of alloy 758 (a) and alloy 833 (b) in the normalized (1 473 K/1.5 h) and air quenched state with the corresponding EDX-spectra of the primary nitrides.

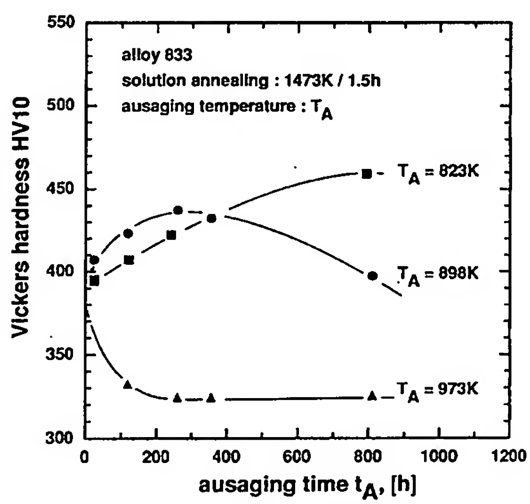


Fig. 3. Isothermal ausage hardening curves of alloy 833.

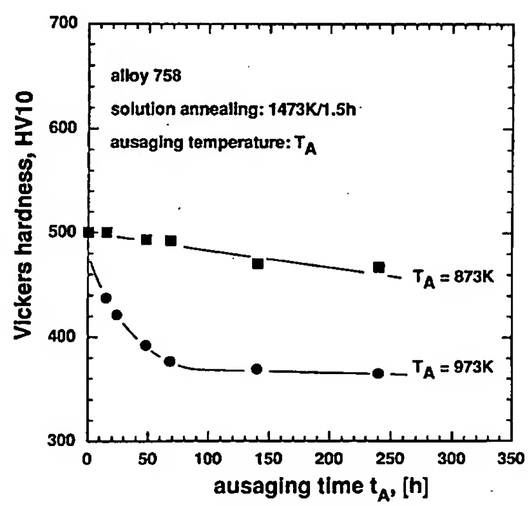


Fig. 4. Isothermal ausage hardening curves of alloy 758.

the laths in one dimension (see also Fig. 14(a)).

3.2. Precipitation and Softening Behaviour during Tempering of the Martensite

3.2.1. Structure and Composition of the Precipitating Phases

Figure 6 shows the selected area electron diffraction pattern of three precipitation states in tempered martensite. The first of them, characterised by a streaked diffraction pattern in the ⟨001⟩ zone of the ferrite has already been observed in nitrided ferritic steels containing Cr, V, Ti, Nb, Mo or W.[11,12] This diffraction pattern reflects a uniform and dense distribution of thin plates or discs on the {100} planes of the ferrite with the Bain orientation relationship[12]:

$$(001)_{b.b.c.} \parallel (001)_{f.f.c.} : [100]_{b.b.c.} \parallel [110]_{f.c.c.}$$

The corresponding diffraction pattern can be consistently indexed with respect to an ideal coherent diffraction pattern from f.c.c.-precipitates with a lattice constant of 0.410 nm. A calculated diffraction pattern based on this assumption is shown in **Fig. 7(a)**. The plate morphology

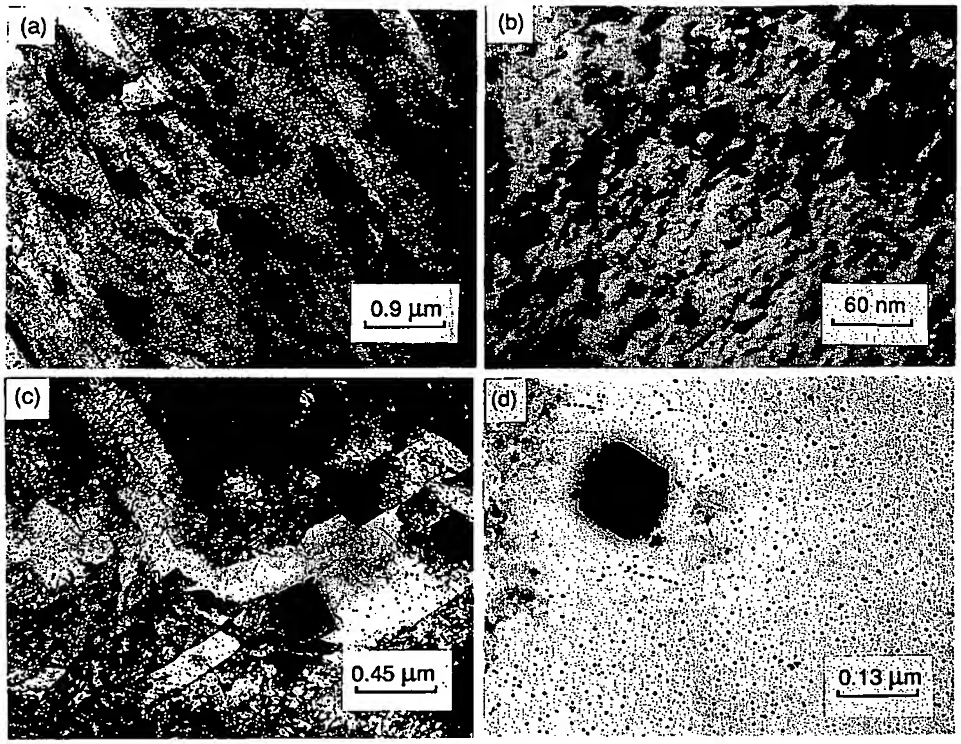
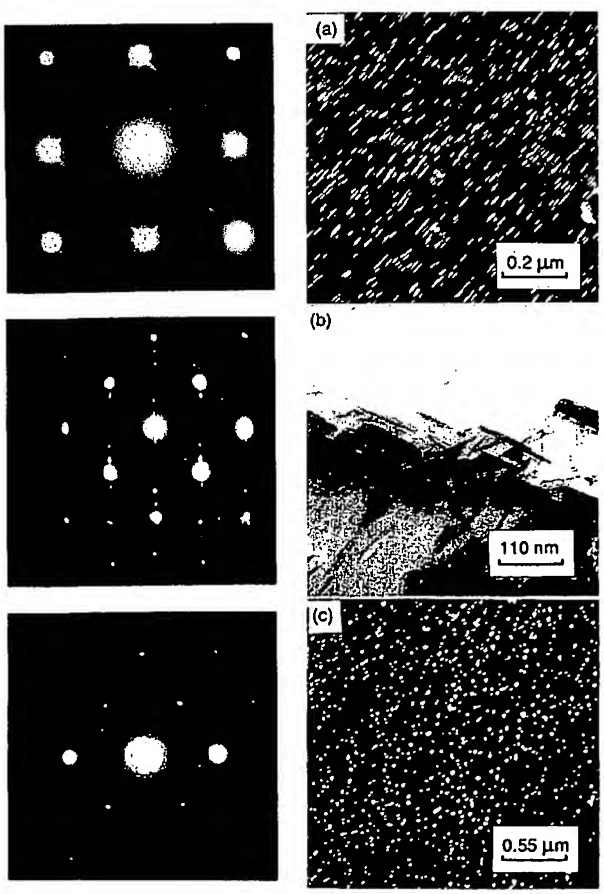


Fig. 5. Transmission electron micrographs of ausaged alloy 833.
(a), (b): ausaged (898 K/260 h) (c), (d): ausaged (973 K/120 h)



of these precipitates can be well recognized in their "over-aged" state shown in Fig. 6(b). This diffraction pattern coming from equally oriented plates located on a subgrain boundary is identical with respect to the Bain orientation relationship. A slight deviation of the double diffraction spots from the (002) direction of the matrix is assumed to be caused by the increased lattice mismatch between the matrix and the large plates. The lattice constant of the f.c.c.-nitrides CrN, VN and NbN is larger than 0.410 nm, for example f.c.c.-CrN has a lattice constant of 0.414 nm. The streaked diffraction pattern of Fig. 6(a) is the commonly observed one in the early tempering states of both alloys at about 973 K. The Bain orientation relationship during tempering is further maintained when the precipitation state is brought into a "peak-aged" state in the austenite before the martensitic transformation. However the Bain orientation relationship was not found during tempering of the "over-ausaged" precipitation state of alloy 833. Figure 6(c) shows the selected area diffraction pattern of such a precipitation state with $[110]_{f.c.c.}$ zone axis in a high order zone of the ferrite as suggested from the calculated diffraction pattern shown in Fig. 7(b).

Fig. 6.
Electron diffraction patterns and corresponding precipitation states:
(a) alloy 758: ausaged (873 K/160 h) and tempered (973 K/4 h), dark-field, $(002)_{f.c.c.}$-centered
(b) alloy 758: ausaged (873 K/160 h) and tempered (973 K/ 360 h)
(c) alloy 833: ausaged (973 K/120 h) and tempered (981 K/4 h), dark field, $(111)_{f.c.c.}$-centered

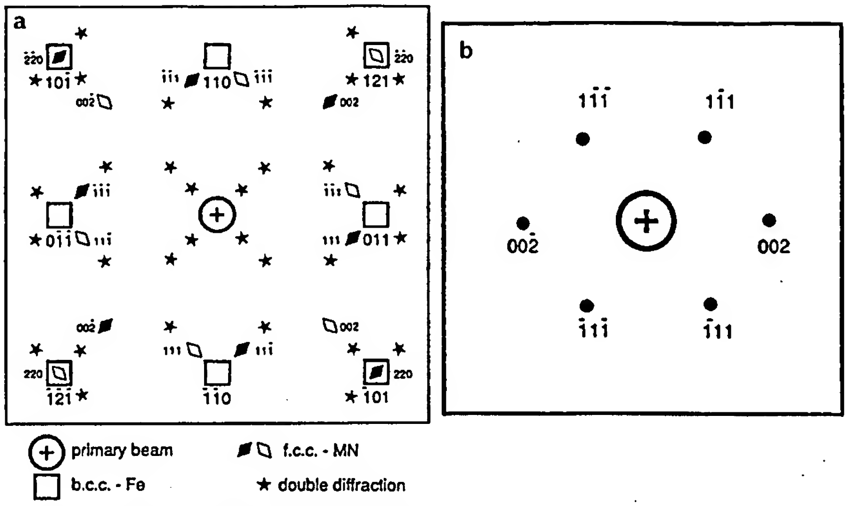


Fig. 7. Calculated diffraction pattern from Figs. 6(a) and 6(c) for lattice constant 0.29 nm (b.c.c.-matrix) and 0.41 nm (f.c.c.-MN).

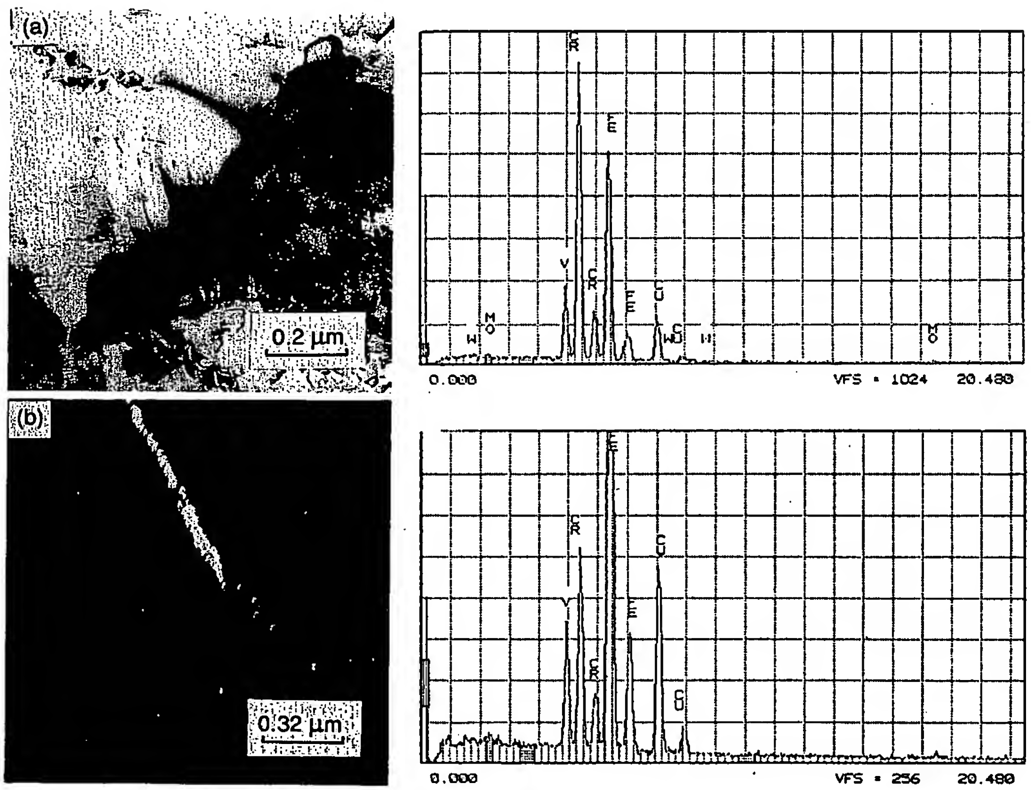


Fig. 8. Electron micrographs of precipitation phases and corresponding EDX-spectra.
(a) alloy 758: normalized and tempered (973 K/4 h)
(b) dark field of alloy 833: $(002)_{f.c.c.}$-centered corresponding to a diffraction pattern of the type shown in Fig. 7(a), normalized and tempered (981 K/28 h)

From the diffraction investigations all of the fine precipitates detected within the subgrains and on the small-angle grain boundaries of the tempered martensite are assumed to be of the f.c.c.-MN type. In addition to this phase, in alloy 758 coarse chromium rich M_2N phase with hexagonal crystal structure could be identified by means of electron diffraction and energy dispersive X-ray analysis (EDX). However, it was not detected in alloy 833 during tempering at 981 K for up to 28 h. Due to small size of the precipitates in alloy 833, increased contribution from the matrix had to be taken into consideration by the interpretation of the EDX-spectra. However, their slow growth behaviour on the grain boundaries and their strong V-signal compared with the Cr-signal in the EDX-spectra suggested that they are of the f.c.c.-MN type. **Figure 8** shows typical EDX-spectra of the precipitates. Figure 8(b) shows a dark field image of a film like precipitate along a subgrain boundary and

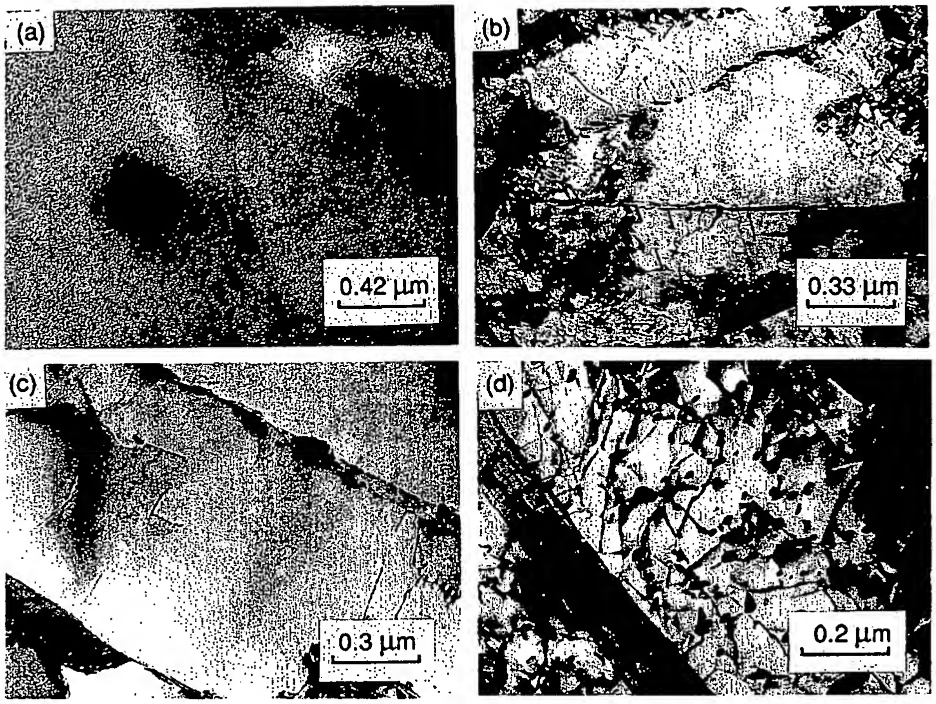


Fig. 9. Precipitation states in (ausaged) and tempered alloy 833.
(a): normalized and tempered (981 K/4 h)
(b): normalized, ausaged (898 K/260 h) and tempered (981 K/ 4 h)
(c): normalized and tempered (981 K/28 h)
(d): normalized, ausaged (973 K/120 h) and tempered (981 K/28 h)

an EDX-spectrum taken from it.

3.2.2. Evolution of the Precipitation States during Tempering

Figure 9 shows various precipitation states of alloy 833 developed during tempering at 981 K up to 28 h for different preheat treatments. Early precipitation states during tempering are found to be very dense and uniform as discussed by their corresponding diffraction pattern before. The following time dependent microstructural evolution is characterised by a progressive decrease of the particle and dislocation density within the subgrain and the development of a recovered and particle stabilized dislocation substructure. Figure 9(c) shows a representative subgrain of the microstructure, normalized and tempered for 28 h. From the micrograph one can see that the precipitates are mainly located on the boundaries of a well recovered subgrain structure. The precipitation density strongly varies from subgrain boundary to subgrain boundary, from no precipitates to film like covering as shown in Fig. 8(b). It is assumed that various interacting processes are responsible for the evolution of non uniform precipitation states which can be observed within 4 h tempering. As an example, Fig. 9(a) shows a particle depleted zone near a primary nitride. Such a zone suggests a low nitrogen concentration around the primary nitride which may already exist before tempering. On the same micrograph one can see further particle depleted zones near internal interfaces. These zones are assumed to be caused by segregation of nitrogen to subgrain boundaries at the beginning of tempering. In Fig. 9(b) it is further demonstrated that an initially "peak-ausaged" precipitation state of alloy 833 is unstable with respect to the evolution of non uniform precipitation states during tempering. This behaviour suggests that, in addition to segregation effects, competetive particle growth between precipitates formed within subgrains and those on the subgrain boundaries is responsible for developing non uniform distribution of precipitates at later tempering stages. This coarsening behaviour is assumed to be favoured by the initially high dislocation density. Dislocation core diffusion paths from the subgrain interior to the surfaces may strongly contribute to an accelerated depletion of fine precipitates within subgrains. On the contrary, an initially "over-ausaged" precipitation state is found to be highly stable and it develops uniform distribution of precipitates as shown in Fig. 9(d). In this case the long-term competetive particle growth is mainly observed among the precipitates already formed in the austenite.

Figure 10 shows structural changes in alloy 758 tempered at 973 K for up to 4 h. In this alloy the evolution of non uniform distribution of precipitates is mainly caused by rapid coarsening of hexagonal chromium nitrides at martensite block boundaries and grain boundaries which are represented with respect to size and morphology in Fig. 10(a). The EDX-spectrum in Fig. 8(a) demonstrates that this phase dissolves a high amount of vanadium. The precipitation density within subgrains is small in the normalized and tempered condition compared with that in an initially ausaged and

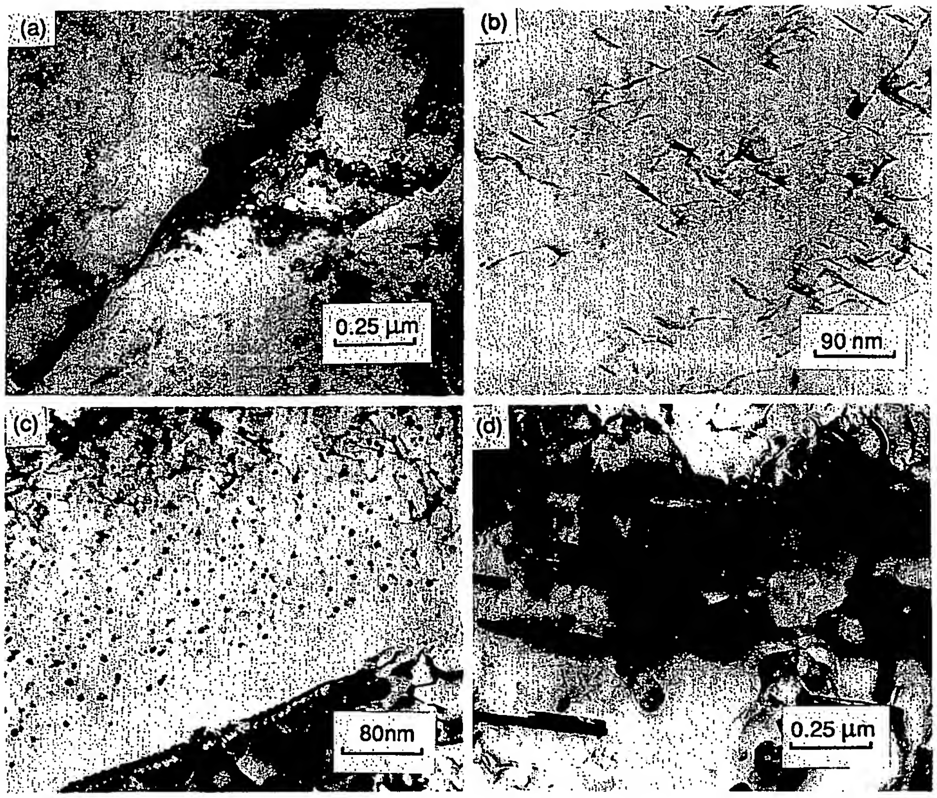


Fig. 10. Precipitation states in (ausaged) and tempered alloy 758.
(a), (b): normalized and tempered (973 K/4 h)
(c): normalized, ausaged (873 K/68 h) and tempered (973 K/2 h)
(d): normalized, ausaged (873 K/68 h) and tempered (973 K/4 h)

tempered condition as shown in Figs. 10(b) and 10(c) respectively. An initially "peak-ausaged" precipitation state in the austenite can maintain its uniformity for several 10 h during tempering in the ferrite range although these precipitation states are still far away from the true phase equilibrium. Formation of hexagonal chromium nitride and a simultaneous dissolution of the face centered cubic nitrides could be observed to occur in a few regions during tempering the ausaged specimen. An example for a local instability of this kind is shown in Fig. 10(d). However, the volume fraction of the hexagonal chromium nitride after normalizing, ausaging and tempering was found to be distinctly smaller than after normalizing and tempering. From these observations it is concluded that the precipitation state produced in the austenite becomes metastable in the ferrite. The formation of heterogeneously distributed hexagonal chromium nitride during tempering of the ausaged specimen further suggests that the evolution of metastable into equilibrium precipitation states depends not only on compositional but also on morphological factors such as the density and the distribution of block boundaries as well as the volume fraction and the stability of the retained austenite.

3.2.3. Softening Behaviour during Tempering

Figure 11 shows the softening of the microstructure during isothermal tempering at 981 K in alloy 833. A continuous softening is observed in the initially nor-

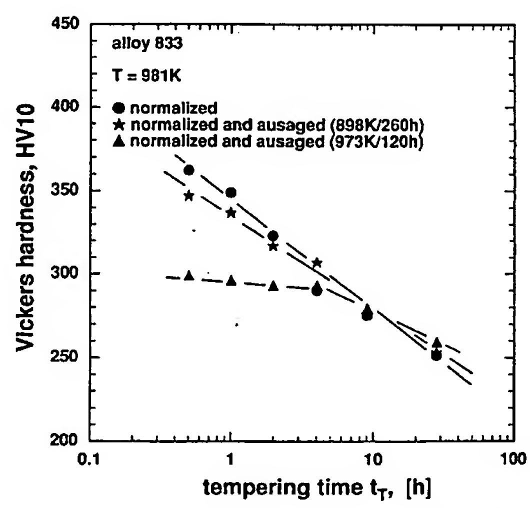


Fig. 11. Isothermal softening curves of alloy 833 at 708°C.

malized state as well as in the initially "peak-ausaged" martensitic state. A discontinuous softening is observed in the initially "over-ausaged" martensitic state. From microstructural investigations it follows that softening proceeds by the precipitation of nitrogen, subsequent coarsening of nitrides and the recovery of dislocations, the latter being retarded by precipitation reactions at the beginning of tempering. As shown previously by the ausaging experiments, hardening of the martensite im-

plies uniform precipitation of nitrides with a size lying in the nanometer range. Although the "peak-ausaged" martensitic state had a higher initial hardness compared to the merely normalized state, its precipitation state did not influence the softening rate during tempering. In this case retardation of dislocation recovery due to the "peak-ausaged" precipitation state at the beginning of tempering becomes compensated by the earlier onset of over-aging processes. The same considerations may be applied to the discontinuous softening of the "over-ausaged" martensitic state. **Figure 12** shows the time dependent particle growth during tempering of the "over-ausaged" precipitates as measured from dark field images. The data fit well the r^3-law for particle coarsening[13,14] at longer tempering time and one can see that the coarsening resistance of the uniformly distributed f.c.c.-nitrides is similar to the γ'-phases in the nickel base alloys.[15] The faster particle coarsening at the beginning of tempering suggests that the concentration of nitrogen in the matrix decreases with tempering time. Lower softening rates at the beginning of tempering may be explained by a contribution of nitrides precipitated in the ferrite. Higher coarsening rate of the "over-ausaged" nitrides then results from

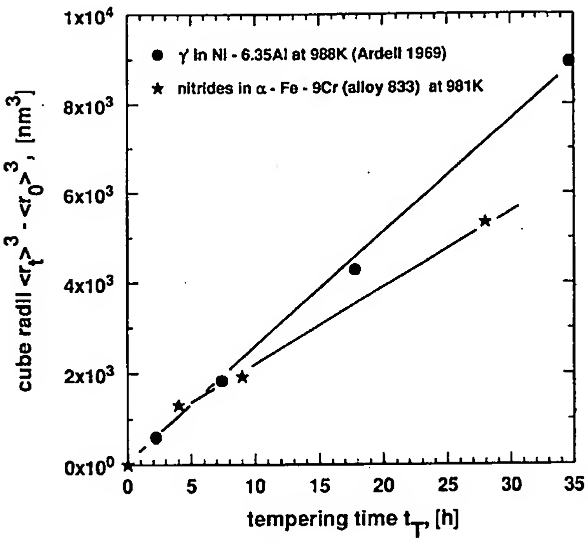


Fig. 12. Coarsening of nitrides in normalized and ausaged (973 K/120 h) alloy 833 during tempering at 981 K in comparison with γ'-precipitates in a Ni-base alloy as measured by Ardell.[15]

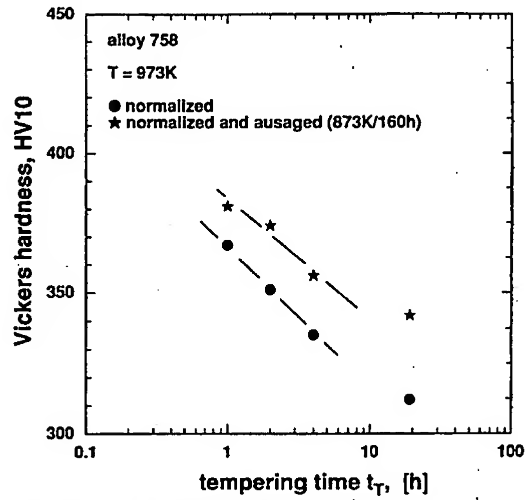


Fig. 13. Isothermal softening curves of alloy 758 at 700°C.

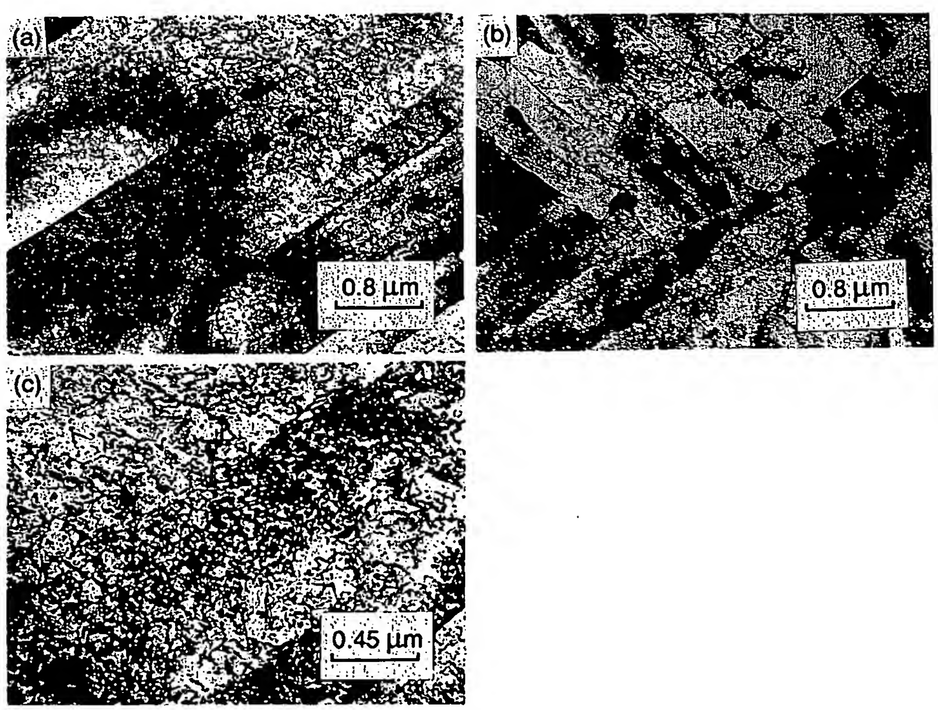


Fig. 14. Precipitation states in (ausaged) and tempered alloy 758.
(a), (c): normalized, ausaged (873 K/160 h) and tempered (973 K/4 h)
(b): normalized and tempered (973 K/4 h)

an increased competetive particle growth between large nitrides formed in the austenite and small nitrides formed in the ferrite. It is worth mentioning that no subgrain growth within this tempering time could be observed. The softening behaviour presented here reflects the resistance to matrix dislocation recovery caused by uniform and dense precipitation states on a very small size scale.

Figure 13 shows the softening of Alloy 758 during isothermal tempering at 973 K. The hardness change indicates the occurrence of partial re-austenitisation during long-term tempering that have to be taken into consideration when discussing the stability of precipitates. In this alloy a slight "over-ausaging" treatment at an ausaging temperature of 873 K has a distinct effect on the tempering resistance irrespective of similar initial hardness level of the martensitic state. An explanation for this behaviour can be found in the martensite morphology and its effect on the stability of the precipitation state. The density of the block boundaries seems to be higher in the normalized and tempered state than in the additionally ausaged state as shown in **Fig. 14**. These boundaries act as nucleation sites for the fast growing hexagonal chromium nitride, thereby decreasing the global precipitation density.

4. Conclusions

Precipitation behaviour and stability of nitrides were investigated in different heat treatments in two high nitrogen martensitic 9–12% steels. The results are the followings.

(1) The precipitation of f.c.c.-nitrides in high nitrogen martensitic 9–12% chromium steels occurs very uniformly and densely in the austenite as well as in the tempered martensite.

(2) The stabilizing effect of Nb could be mainly recognized in a retardation of particle coarsening of the nitrides during ageing in the austenite. It allows grain size control at high normalizing temperatures and ausage hardening of the martensite at intermediate temperatures.

(3) The hardness of the as-quenched martensite and the softening kinetics at the early tempering stages sensitively depend on the size of nitrides in the nanometer range.

(4) Proper ausaging treatment was found to be an effective tool to control uniform particle distribution and the phase evolution of dense particle/dislocation substructures in tempered martensite.

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